Short communication

Effect of tris(trimethylsilyl)borate on the high voltage capacity retention of LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$/graphite cells

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HIGHLIGHTS

► TMSB is evaluated as an electrolyte additive in LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ based cell at high voltage.
► A thinner cathode electrolyte interface can be formed using TMSB in the electrolyte.
► The combination of TMSB with anion can lower the interfacial impedance.
► The cycle performance of LIBs (3.0–4.4 V) can be improved using this additive.

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ABSTRACT

This study demonstrates that tris(trimethylsilyl)borate (TMSB) additive in the electrolyte can dramatically improve the cycling performance of LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$/graphite cell at higher voltage operation. And the effects of this additive are characterized by linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM). In the voltage range of 3.0–4.4 V, LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$/graphite cell with TMSB in the electrolyte retains about 92.3% of its initial capacity compared to the cell without additive in the electrolyte that retains only 28.5% of its initial capacity after 150 cycles, showing the promising prospect of TMSB at higher voltage. The enhanced cycling performance is attributed to the thinner film originated from TMSB on the LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ and the combination of TMSB with PF$_6^-$ and F$^-$ in the electrolyte, which not only protects the undesirable decomposition of EC solvents but also results in lower interfacial impedance.

1. Introduction

Layered transition-metal oxides, including LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$, LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$, LiNi$_{0.4}$Co$_{0.4}$Mn$_{0.2}$O$_2$, have been widely investigated as prospective cathode materials of lithium ion battery (LIB), because of their lower cost, higher capacity, better thermal stability, and less toxicity than commercialized LiCoO$_2$ material [1,2]. Recently, with the development of high-energy density consuming electric devices, more efforts have been paid on these layered transition-metal oxides cathode materials to further improve their electrochemical performance, especially higher capacity and cycle performance [3,4]. One method of enhancing the reversible capacity of LIB is to increase the range of operating voltage of the cells [5,6]. However, naturally unstable Ni^{3+} ions are active at higher voltage, which can easily catalyze the oxidative decomposition of the electrolyte and ultimately lead to the poor cycling efficiency of the battery [7].

The problems associated with reactions of the electrolyte on the surface of high voltage cathode materials have been reported to limit the application of these materials. In order to suppress decomposition of electrolyte and stabilize these layered transition-metal oxides cathode structure, some approaches have been studied, typically coating metal oxide particles on cathode surface [8–10]. The surface modified cathodes have better rate capability or cycle life compared to the uncoated cathodes, however, a noticeable capacity decay were still observed in the following cycles at higher operating voltage. In addition, it was found that the cathode electrolyte interface (CEI) film can be formed on the cathode surface, and the properties of the film plays an important role in determining battery performance, including cycle life, coulombic efficiency, and irreversible capacity, especially at higher voltage operation [11]. Therefore, an alternative approach using sacrificial

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electrolyte additives for the formation of a higher qualitative CEI film has also been reported to be an effective and economic method for the improvement of LIB performance at higher voltage. Some organic and inorganic additives exhibited positive effects in $LiCoO_2$ based [5,12,13] and $LiNi_{0.5}Mn_{1.5}O_4$ based lithium ion battery [14,15]. These additives participate in the formation process of the CEI film, and then suppress the decomposition of electrolyte at higher voltage. Also, these results suggest that modified surface components play an important role in the performance of the CEI layer at higher voltage.

Anion receptors, which display a strong coordination with anions, prevent the decomposition reaction of anions and even dissolve LiF in the electrolyte, have been proposed as new electrolyte additives for LIB [16–19]. Therein, as an electron-deficient boron compound and anion receptor, tris(trimethylsilyl)borate (TMSB) can easily combine with electron-rich materials, and has been positively considered as an electrolyte additive to improve performance of $LiFePO_4$-based LIB at evaluated temperature [20]. The combination of TMSB with anions will improve the thermal stability of $LiPF_6$ salts and hence increase the performance of LIB at 55 °C.

In line with these, we expected that TMSB can also effectively function as an additive to improve the capacity retention of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ based LIB at high operating voltage. In this paper, the effects of the TMSB additive on the modification of CEI layer and the electrochemical performance of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cycled in the 3.0–4.4 V were studied by electrochemical impedance spectroscopy (EIS), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), as well as battery performance test.

2. Experimental

2.1. Preparation

The additive, tris(trimethylsilyl)borate (TMSB), was purchased from Fujian Chuangxin Science and Technology Develops Co. Ltd. (China), and used without further purification. A mixture of ethylene carbonate (EC)/ethyl methyl carbonate (EMC) (1:2, wt.%, Guangzhou Tinci Materials Technology Co. Ltd, China) containing 1 mol L^{-1} $LiPF_6$ was used as the stand electrolyte. The commercial materials were used to prepare the $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cathode and the graphite anode, and then to fabricate the rectangular unit cells to evaluate the real effects of TMSB on the electrochemical performances of LIBs at 4.4 V cut-off voltage. The cathode electrode with an active mass loading of about 3.3 mg cm^{-2} was prepared by combining 89 wt.% $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ (Tianjiao Technolgy Co. Ltd, Shenzhen, China), 6 wt.% acetylene carbon black and 5 wt.% PVDF binder, coating on Al foil. The anode with an active mass loading of about 1.9 mg cm^{-2} was prepared by mixing 95 wt.% natural graphite, 2 wt.% sodium carboxymethyl cellulose (CMC), and 3 wt.% styrene butadiene rubber (SBR). Both electrodes were dried at 120 °C for 10 h under vacuum condition prior to assembly.

2.2. Characterization

Linear sweep voltammetry (LSV) was carried out using Instrumental Electrochemical Workstation (CHI660, Chenhua, Shanghai) on a platinum working electrode with lithium counter and reference electrodes at a scan rate of 0.1 mV s^{-1}. The unit cells were charged to 4.2 V or 4.4 V at constant-current of 1 C, followed by a constant potential until the current reached 0.05 C, and then discharged to 3.0 V at constant-current on battery charger testing device (BS-9300R, Qingtian, Guangzhou).

The electrochemical impedance spectra (EIS) of the cells charged to 4.4 V after one cycle and 150 cycles were measured with frequency response analyzer (FRA, Solartron 1455A, England). Frequency of impedance ranges from 100 kHz to 0.01 Hz at an amplitude of 10 mV.

To analyze the composition of the electrodes after charge–discharge cycling measurements, the cells were disassembled in a glove box under Ar atmosphere. The $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ electrodes were rinsed with anhydrous dimethyl carbonate (DMC) solvent 3 times to remove residual EC and $LiPF_6$, followed by dried under vacuum condition for 12 h at room temperature. The element composition on the surface of cathode was analyzed by X-ray photoelectron spectroscopy (XPS, Axis Ultra DLD, Kratos) with Al Kα line as an X-ray source. The graphite peak at 284.3 eV was used as a reference for the final adjustment of the energy scale in the spectra. Transmission electron microscopy (TEM, JEM-2100, JOEL, Japan) was used to characterize the surface morphology of the cathode powder.

3. Results and discussion

3.1. Electrochemical performance of TMSB

As reported in the previous studies, the additive for the cathode, should have a lower oxidation potential to the main solvents [21,22]. In order to evaluation of the possibility of TMSB as the cathode additives, the oxidation potential of TMSB in the electrolyte was measured by LSV at Pt electrode with three-electrode cell. As shown in Fig. 1(b), a oxidative current peak is observed at 5.0 V (vs. Li/Li$^+$) before solvent decomposition, while the corresponding current peak is not observed for the electrolyte without TMSB in Fig. 1(a). The result indicates that the TMSB is easier to be oxidized at higher potential than the solvents, and may be take part in the formation of interface layer on the cathode surface. As a consequence of the electrochemical oxidation behavior, the CEI layer originated from the TMSB oxidation may effectively suppress electrolyte decomposition on the cathode under higher voltage operation.

The formation cycles of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$/graphite cells were carried out by two charge–discharge cycles at 0.2 C. Fig. 2 shows the first charge–discharge curves of two cells with or without 0.5 wt.% TMSB in the electrolyte. It can be seen that the discharge capacity and coulombic efficiency of the cell without TMSB are 172.2 mAh g^{-1} and 85.9%, respectively. For the cell with TMSB, the discharge capacity in the first cycle is 181.0 mAh g^{-1} with a coulombic efficiency of 90.1%, showing TMSB can increase the initial capacity and coulombic efficiency of LIBs.
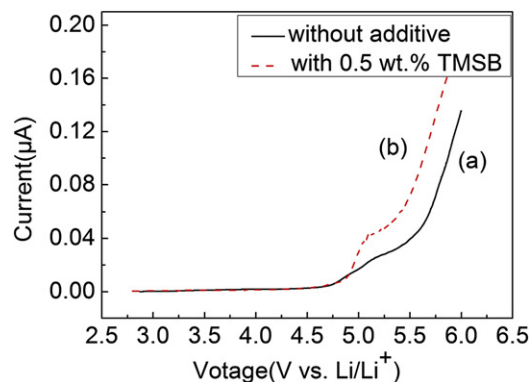

Fig. 1. Linear sweep voltammograms of Pt electrodes in 1 mol L^{-1} $LiPF_6$–EC:EMC (1:2) (a) without additive, (b) with 0.5% TMSB between open circuit voltage (OCV)-6.0 V at 0.1 mV s^{-1}.
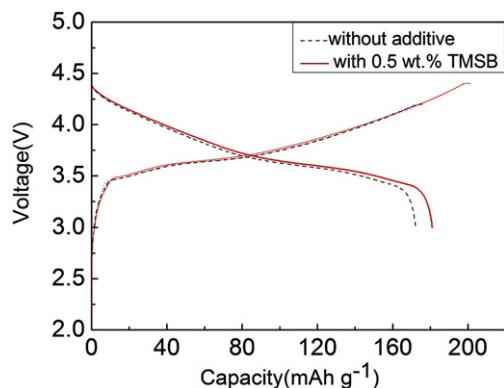
Fig. 2. The first charge and discharge curves of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$/graphite cells with and without TMSB in the electrolyte, the charge and discharge rate was 0.2 C in the potential range of 2.5–4.4 V.

After formation cycles at 0.2 C, the cells were cycled at 1.0 C over the range of 3.0–4.2 V, and 3.0–4.4 V respectively. As shown in Fig. 3 and Fig. 4, it is observed that about 15% increased discharge capacity is realized by extending the charge potential beyond the traditional 4.2 V limit to 4.4 V. The cells with and without TMSB exhibit almost identical cycling performance and efficiency when they are cycled in the potential range of 3.0–4.2 V. However, with increasing the cut off voltage to 4.4 V, the capacity retention and efficiency of the cells were found to depend on the presence of TMSB in the electrolyte. The cell without additive shows a sharply capacity fade from 168.0 mAh g^{-1} to 47.9 mAh g^{-1}, with a capacity retention of 28.5% and a efficiency of 92.8% after 150 cycles, while the capacity of cell with 0.5 wt.% TMSB is 154.9 mAh g^{-1} at the 150th cycle, remains 92.3% of its initial capacity (167.9 mAh g^{-1}). The efficiency maintains 99.9% after 150 cycles. It is apparent that the capacity retention can be significantly improved by using TMSB as additive in the electrolyte. In addition, with increasing the content of additive, the cell with 1.0 wt.% TMSB in the electrolyte show slightly decreased initial capacity and capacity retention than the cell with 0.5 wt.% TMSB. Therefore, the concentration of TMSB added in the electrolyte is ultimately determined to be 0.5 wt.%.

The electrochemical impedance spectra (EIS) of the $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$/graphite cells fully charged to 4.4 V were performed
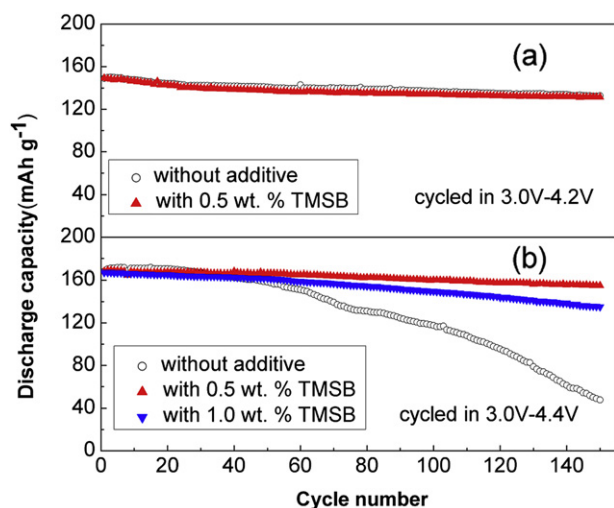

Fig. 4. The coulombic efficiency of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$/graphite cells cycled at 1.0 C in the potential range of (a) 3.0–4.2 V and (b) 3.0–4.4 V.

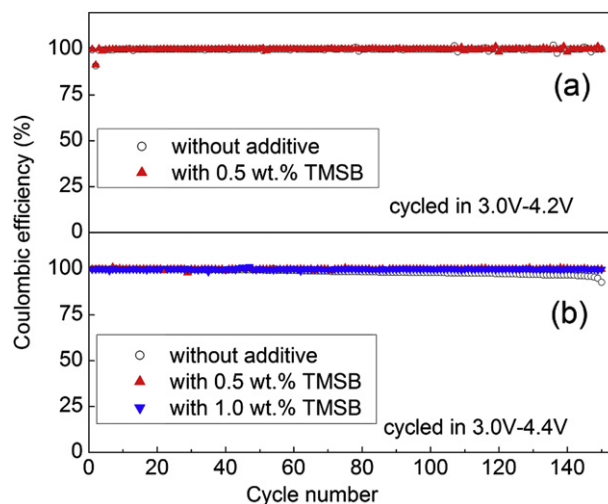to evaluate the effect of TMSB after the first cycle and the 150th cycle, respectively, as shown in Fig. 5. For the cell with TMSB, the first semicircle attributed to the resistance and capacitance of electrolyte interface film of the cathode shows a similar resistance to the cell without additive, whereas the second semicircle assigned to the charge transfer resistance is slightly decreased than that without additive [5,23]. The result is consistent with the cell using TMSB having a higher discharge capacity in the first cycle (Fig. 2). After 150 cycles, the interfacial impedance of the cell without additive is significantly increased, which indicates
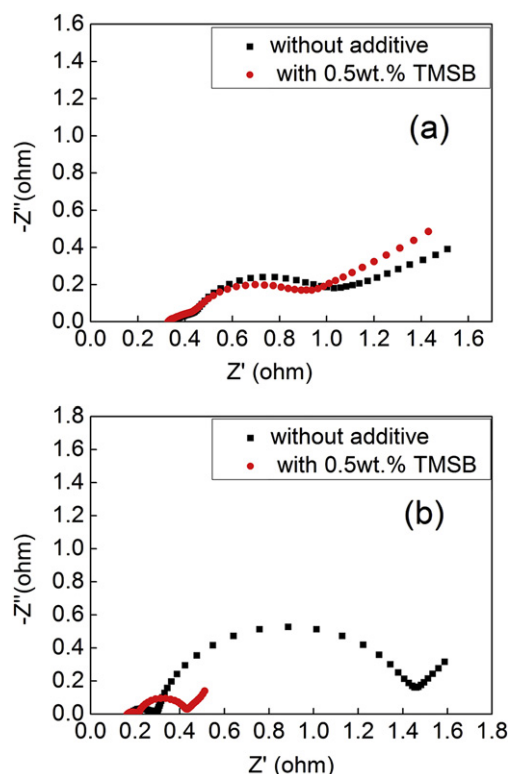

Fig. 3. The cycling performance of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$/graphite cells cycled at 1.0 C in the potential range of (a) 3.0–4.2 V and (b) 3.0–4.4 V.

Fig. 5. EIS patterns of the graphite/$LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cells after (a) the 1st cycle and (b) the 150th cycles.

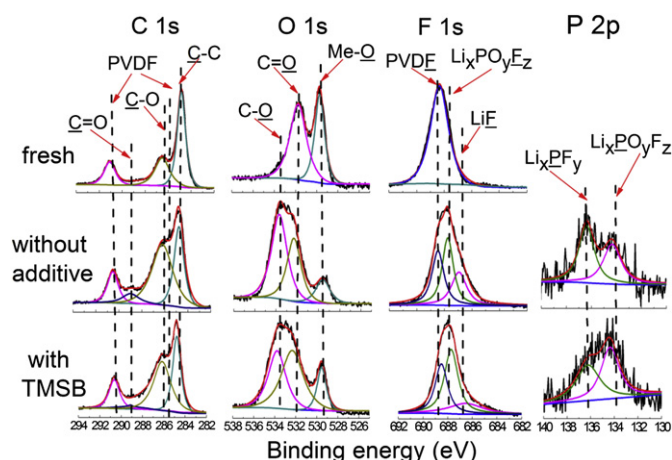**Fig. 6.** XPS patterns of the fresh and the cycled $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ electrodes in the electrolyte without and with 0.5 wt.% TMSB.

a growth of a resistive layer on the electrode surface as electrolyte decomposition at high voltage. More interestingly, the cell with TMSB shows much reduction of interfacial resistance during cycling, as shown in Fig. 5(b). It may be ascribed that the CEI layer morphology derived from TMSB, which was formed in the formation cycling stage, is matured in the subsequent cycles. This might be due to the formation and dissolution of the CEI layer instead of a continuous growth in thickness and density on the cathode surface [24]. Furthermore, it has been reported that the additive based on electron deficient borate or borate compounds would coordinate with anion, such as PF_6^- and F^-, which will enhance the ion pair dissociation of Li^+ and anion, and thus improve the ionic conductivity and lower the interfacial impedance [20].

3.2. XPS of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cathode

To further investigate the contribution of TMSB on the cathode surface modification, the surface chemical composition of the fresh and the cycled cathodes with and without TMSB were determined by XPS, as shown in Fig. 6, and the atomic composition of the surface films is listed in Table 1. Additional Si element and B element are detected in the sample with additive, which implies that the added TMSB may participate in the formation of the interface layer on the $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cathode, and the decomposition products of TMSB modify the components of the surface layer.

The C 1s peak associated with PVDF binder (290.3 eV and 285.7 eV) and graphite (284.8 eV) are presented in all of samples including the fresh and cycled cathodes. Additional signals C=O (289 eV) and C–O (286 eV) appeared in both cycled cells, and the intensity of the peak declined with adding TMSB in the electrolyte. These originate from carbonate groups involved in polymerized carbonates formed by direct polymerization of EC and initiated by EC oxidation [11]. The results of O1s peaks can also be explained by the same reason. Compared to the fresh cathode, the intensity

Table 1
The element concentration determined by XPS on the surface layer of the $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cathodes cycled in 1 mol L^{-1} $LiPF_6$/EC:EMC (1:2) with and without 0.5 wt.% TMSB.

Elements	C 1s	O 1s	F 1s	Mn2p	Ni2p	Co 2p	P 2p	Si 2p	B1s
1#	52.16	15.53	24.66	1.98	4.28	1.39	–	–	–
2#	50.16	21.70	21.71	1.22	3.19	0.89	1.05	–	–
3#	48.28	20.88	21.33	1.5	2.99	0.95	1.26	0.45	2.37

Note: 1# is the fresh cathode; 2# and 3# are cathodes cycled in the electrolyte without and with 0.5 wt.% TMSB, respectively.

peaks characteristic of C–O (533.5 eV) and C=O (531.8 eV) are greatly increased in both cycled samples as would be expected for PEC [14]. Furthermore, comparison of the O1s peaks in the cycled samples indicates that the ratio of relative intensity peak of C=O to C–O is decreased in cell with TMSB, which coincides with the less content of the EC oxidation product [25]. In addition, compared to the sample with TMSB, the smaller quantities of metal oxide (Me–O, 529.5 eV) in cell without additive indicates a thicker film is covered on the surface of the cathode.

Analysis of the F1s spectra provides additional information. The F1s spectra around at 686.5 eV, 688.0 eV, 688.8 eV correspond to the decomposition products of $LiPF_6$ and the C–F of PVDF, respectively [26]. In the case without TMSB, F1s spectrum exhibits an
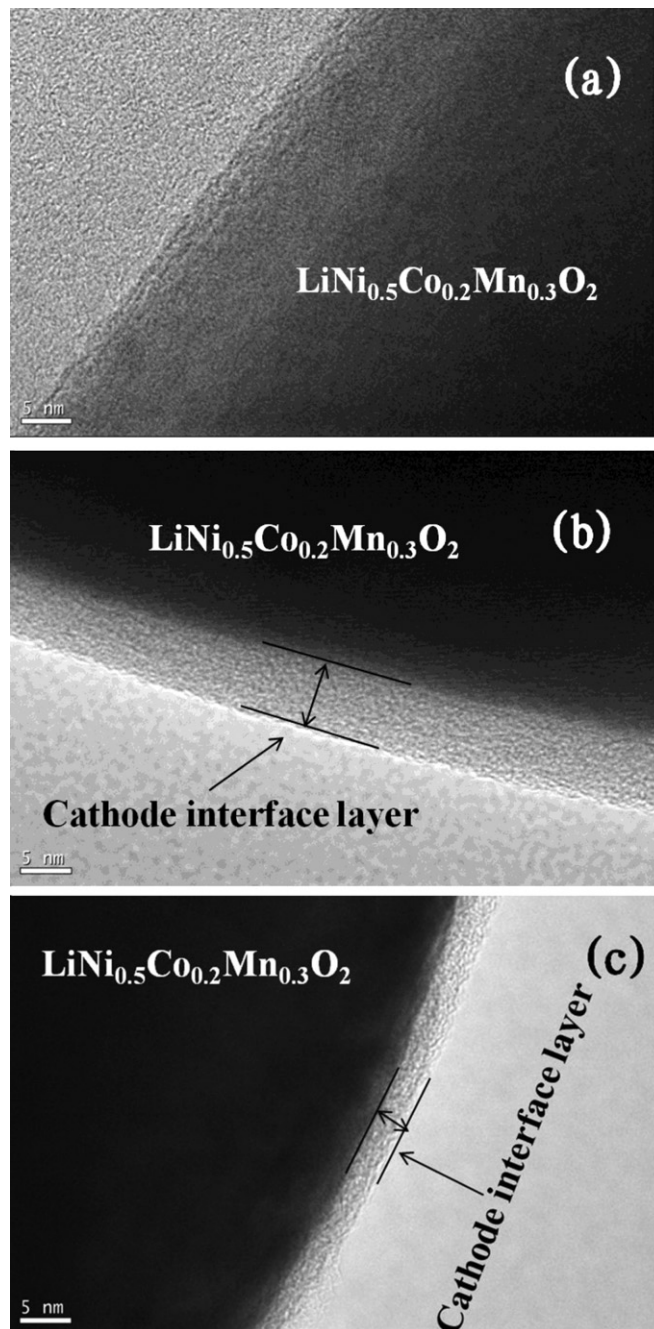

Fig. 7. TEM images of (a) fresh $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cathode powder, and cathodes powder after 150 cycles in the electrolyte (b) without TMSB and (c) with 0.5 wt.% TMSB.
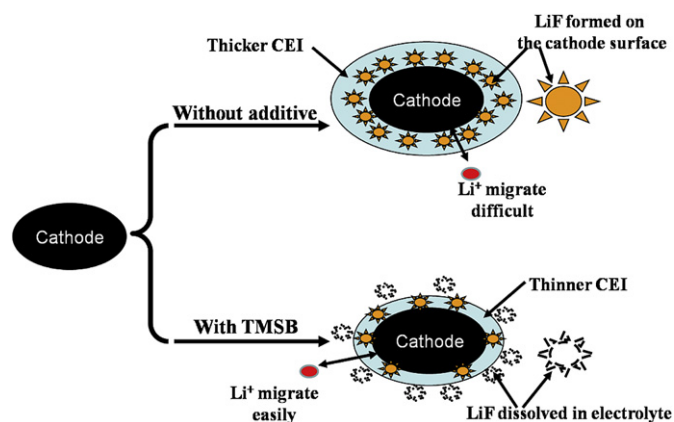
Fig. 8. The fundamental roles of TMSB to enhance the high voltage performance of LIB.

intense shoulder around 686.5 eV corresponding to LiF, which is lower greatly in the case of TMSB addition. It is well known that more content of LiF covered onto the cathodes surface would increase the interfacial impedance, which is also consistent with the interfacial impedance of the cells with TMSB was smaller than that without additive [27].

For the P 2p spectra, both cycled samples showed two P $2p_{3/2}$ peaks, one at 133.7 eV, indicative of $LiP_xF_yO_z$ and another one at 136.5 eV, indicative of LiP_xF_y [28]. It is easily can be seen that the intensity of LiP_xF_y (687.5 eV) is lower for the case with TMSB than that without additive. As has been reported earlier, $LiPF_6$ is known to decompose to PF_5 and LiF , PF_5 in turn reacts with residual water to form HF and PF_3O, the latter can then form LiP_xF_y species [28]. Therefore, the result indicates that the decomposition of $LiPF_6$ is retarded with the addition of TMSB in the electrolyte. This is not surprising, the interaction between TMSB and anion (such as PF_6^- and F^-) improve not only the dissolvability of the LiF in the electrolyte, but also the stability of $LiPF_6$ salts [20]. This combination result in increasing the number of free Li $^+$ and lower the interfacial impedance, and hence improving the performance of the lithium battery at higher voltage operations.

3.3. TEM of LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ electrode

Fig. 7 presents the TEM images of fresh LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ electrode powder and the cycled electrode powder, respectively. From Fig. 7(a), a clear boundary can be observed on the fresh LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ cathode powder. Whereas, the cycled samples show amorphous layers covering onto the cathode surface, which are known to be the CEI, as shown in Fig. 7(b) and Fig. 7(c). Evidently, the CEI derived from the electrolyte containing TMSB shows a layer with a thickness of 3 nm, which is thinner and less compact than that without additive (with a thickness about 10 nm). Combination of TEM images and the result of EIS, the fundamental roles of TMSB to enhance the high voltage performance of LIB is displayed in Fig. 8. It can be supposed that with increasing the number of cycles under high voltage operation, a more and more thick and resistant CEI layer containing LiF is formed, which may not be favor to the migration of lithium ion, thus leading to the rapid drop of the capacity. In comparison, with TMSB in the electrolyte, the electron-deficient boron compound tends to promote the dissolution of LiF at the cathode surface, which results in the

formation of a thinner modified film and the reduction of interfacial resistance between the cathode and electrolyte at the high voltage.

4. Conclusion

TMSB is investigated as an electrolyte additive for the formation of a cathode layer on the LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ electrode at high voltage. The LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$/graphite cell with TMSB exhibited a high initial discharge capacity of 181.0 mAh g^{-1} in the voltage range of 3.0–4.4 V, and its capacity retention were greatly improved compared to that without additive. The result showed that the improved performance of cell is mainly ascribed to the thinner film derived from TMSB that can protect cathode from the undesirable decomposition of EC solvents at higher voltage and the modified components of the CEI on the LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ cathode surface.

References

[1] K. Xu, Chem. Rev. 104 (2004) 4303.
[2] Y.H. Cho, S.H. Lee, Y.S. Lee, T.E. Hong, J. Cho, Adv. Energy Mater. 1 (2011) 821.
[3] M. Jo, S. Jeong, J. Cho, Electrochem. Commun. 12 (2010) 992.
[4] H. Lee, M.G. Kim, J. Cho, Electrochem. Commun. 9 (2007) 149.
[5] K.S. Lee, Y.K. Sun, J. Noh, K.S. Song, D.W. Kim, Electrochem. Commun. 11 (2009) 1900.
[6] A. Abouimrane, I. Belharouak, K. Amine, Electrochem. Commun. 11 (2009) 1073.
[7] Y.S. Lee, D. Ahn, Y.H. Cho, T.E. Hong, J. Cho, J. Electrochem. Soc. 158 (2011) A1354.
[8] J. Liu, A. Manthiram, J. Electrochem. Soc. 156 (2009) A66.
[9] T. Noguchi, I. Yamazaki, T. Numataa, M. Shirakata, J. Power Sources 174 (2007) 359.
[10] B. Kim, J.G. Lee, M. Chio, J. Cho, B. Park, J. Power Sources 126 (2004) 190.
[11] K. Edstrom, T. Gustafsson, J.O. Thomas, Electrochim. Acta 50 (2004) 397.
[12] K. Abe, Y. Ushigoe, H. Yoshitake, M. Yoshio, J. Power Sources 153 (2006) 328.
[13] J.N. Lee, G.B. Han, M.H. Ryou, D.J. Lee, J.C. Song, J.W. Choi, J.K. Park, Electrochim. Acta 56 (2011) 5195.
[14] L. Yang, T. Markmaitree, B.L. Lucht, J. Power Sources 196 (2011) 2251.
[15] A.V. Cresce, K. Xu, J. Electrochem. Soc. 158 (2011) A337.
[16] X. Sun, H.S. Lee, X.Q. Yang, J. McBreen, Electrochem. Solid-State Lett. 5 (2002) A248.
[17] Z. Chen, K. Amine, J. Electrochem. Soc. 153 (2006) A1221.
[18] C.C. Chang, T.K. Chen, J. Power Sources 193 (2009) 834.
[19] Y.M. Lee, Y.G. Lee, Y.M. Kang, K.Y. Cho, Electrochem. Solid-State Lett. 13 (2010) A55.
[20] Z.J. Cai, Y.B. Liu, J.H. Zhao, L. Li, Y.M. Zhang, J. Zhang, J. Power Sources 202 (2012) 341.
[21] K. Abe, T. Hattori, K. Kawabe, Y. Ushigoe, H. Yoshitake, J. Electrochem. Soc. 154 (2007) A810.
[22] M.H. Ryou, G.B. Han, Y.M. Lee, J.N. Lee, D.J. Lee, Y.O. Yoon, J.K. Park, Electrochim. Acta 55 (2010) 2073.
[23] M.D. Levi, G. Salitra, B. Markovsky, H. Teller, D. Aurbach, H. Udo, H. Lilia, J. Electrochem. Soc. 146 (1999) 1279.
[24] Y. Zhang, C.Y. Wang, J. Electrochem. Soc. 156 (2009) A527.
[25] L. Yang, B. Ravdel, B.L. Lucht, Electrochem. Solid-State Lett. 13 (2010) A95.
[26] H. Bryngelsson, M. Stjerndahl, T. Gustafsson, K. Edström, J. Power Sources 174 (2007) 970.
[27] J.H. Park, J.S. Kim, E.G. Shim, K.W. Park, Y.T. Hong, Y.S. Lee, S.Y. Lee, Electrochem. Commun. 12 (2010) 1099.
[28] H. Duncan, D. Duguay, Y.A. Lebdeh, I.J. Davidson, J. Electrochem. Soc. 158 (2011) A537.